Earth Science Technology Conference - 2005

New Laser Techniques for Detection of Radicals, Isotopes, and Reactive Intermediates from Robotic Aircraft and Conventional Aircraft for the Aura Satellite Collaborative Science Effort

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June 28, 2005

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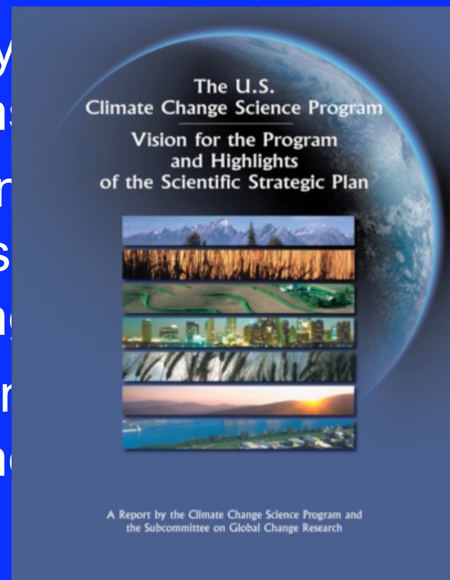
Presidential Initiatives

- US Climate Change Science Program: Strategic Plan
  1. Reduce uncertainty … ow the Earth's climate and related system … e future;
  2. Understand the ser … bility of different natural and managed ecos … systems to climate and related global chan
  3. Explore the uses ar … of evolving knowledge to manage risks an … ted to climate variability and change



- Global Earth Observation Initiative: 2003

NRC Decadal Report Requested by NASA and NOAA

PHASE I

Earth Science and Applications from Space:

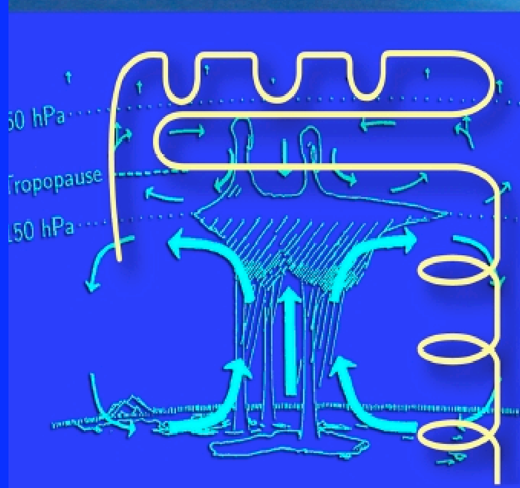
Urgent Needs and Opportunities to Serve the Nation

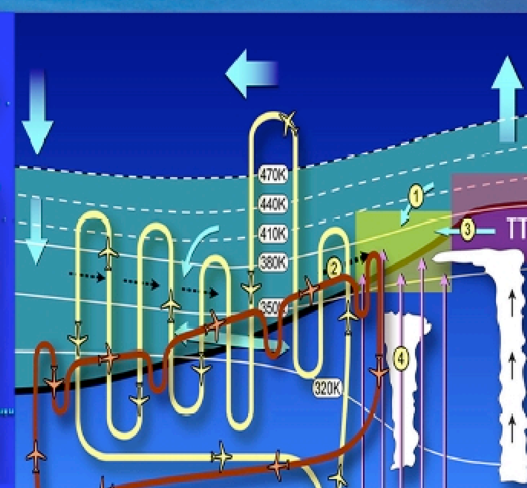
Explicitly Identify the Critical Importance of Societal Objectives

Emphasize the Required Decision Support Structure

AURA Collaborative Science: Proposed *in situ* Airborne Observations, Hypotheses and Deployment Strategy in Support of UARP

June 2003

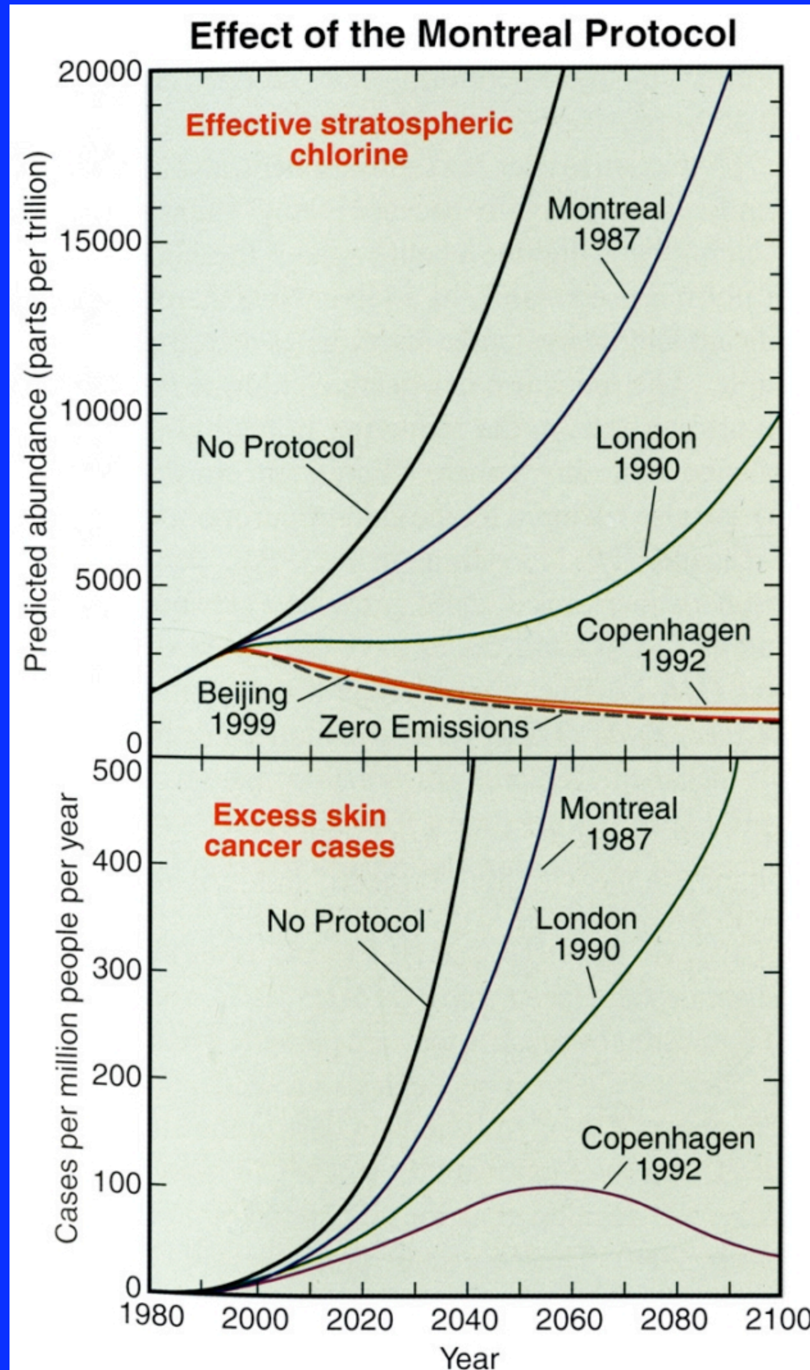




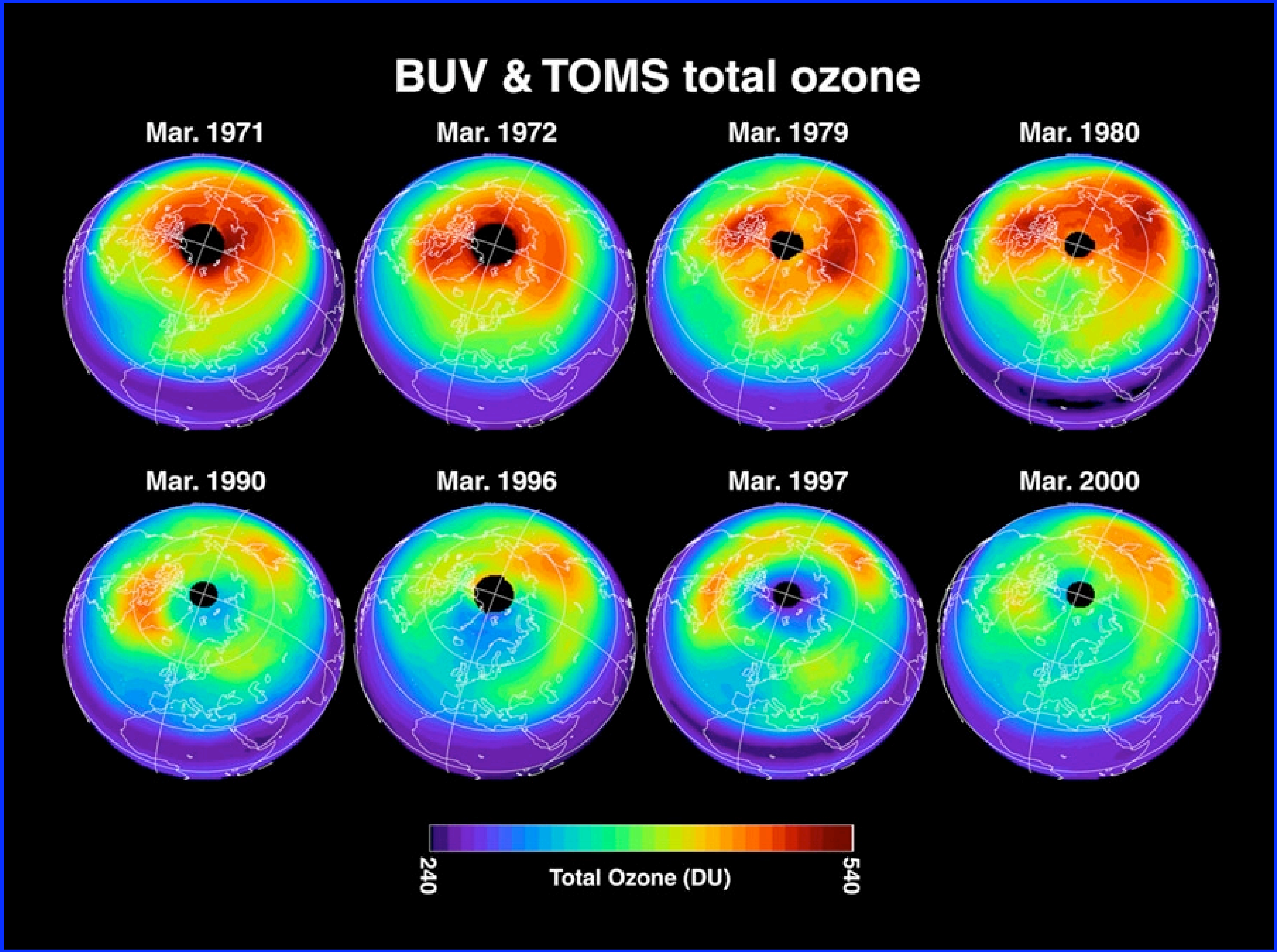

NASA
AURA

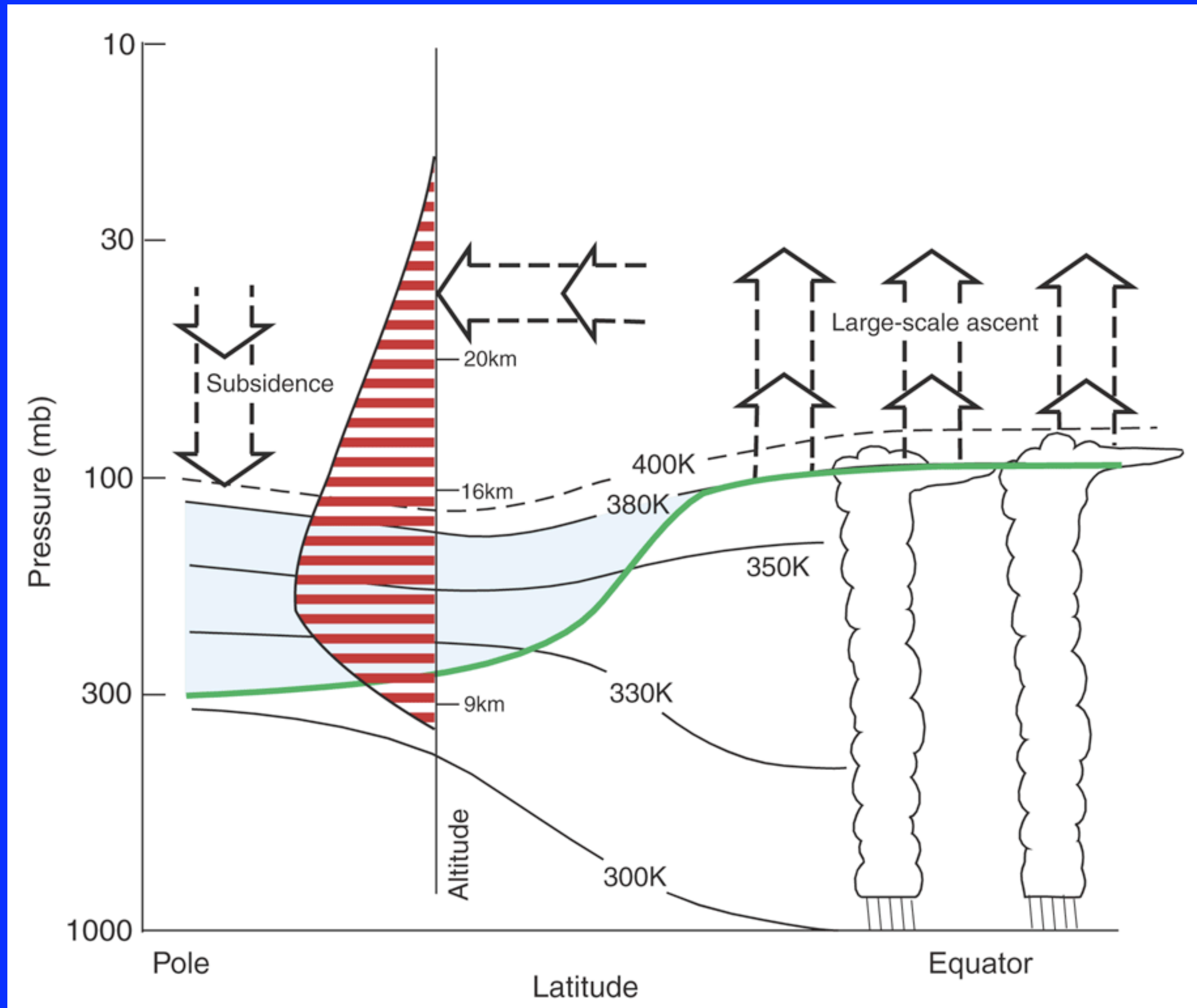
Four Primary Focus Areas

- Decadal Forecast of UV Dosage Levels
- Linking Nitrate, Sulfate, Heavy Metal, and Organic Source Strengths, on a Global Scale, to Changes in the Optical Properties of the Atmosphere, a.k.a. Short-Wave Forcing
- The Aura Satellite Collaborative Science Endeavor
- Technology Innovation for the UAV - Small Satellite Era


Effect of the Montreal Protocol
Effective stratospheric chlorine
Predicted abundance (parts per trillion)
20000
15000
10000
5000
0
Montreal 1987
No Protocol
London 1990
Copenhagen 1992
Beijing 1999
Zero Emissions
Excess skin cancer cases
Cases per million people per year
500
400
300
200
100
0
Montreal 1987
No Protocol
London 1990
Copenhagen 1992
1980
2000
2020
2040
2060
2080
2100
Year

Ozone Loss in Northern Hemisphere from Satellite

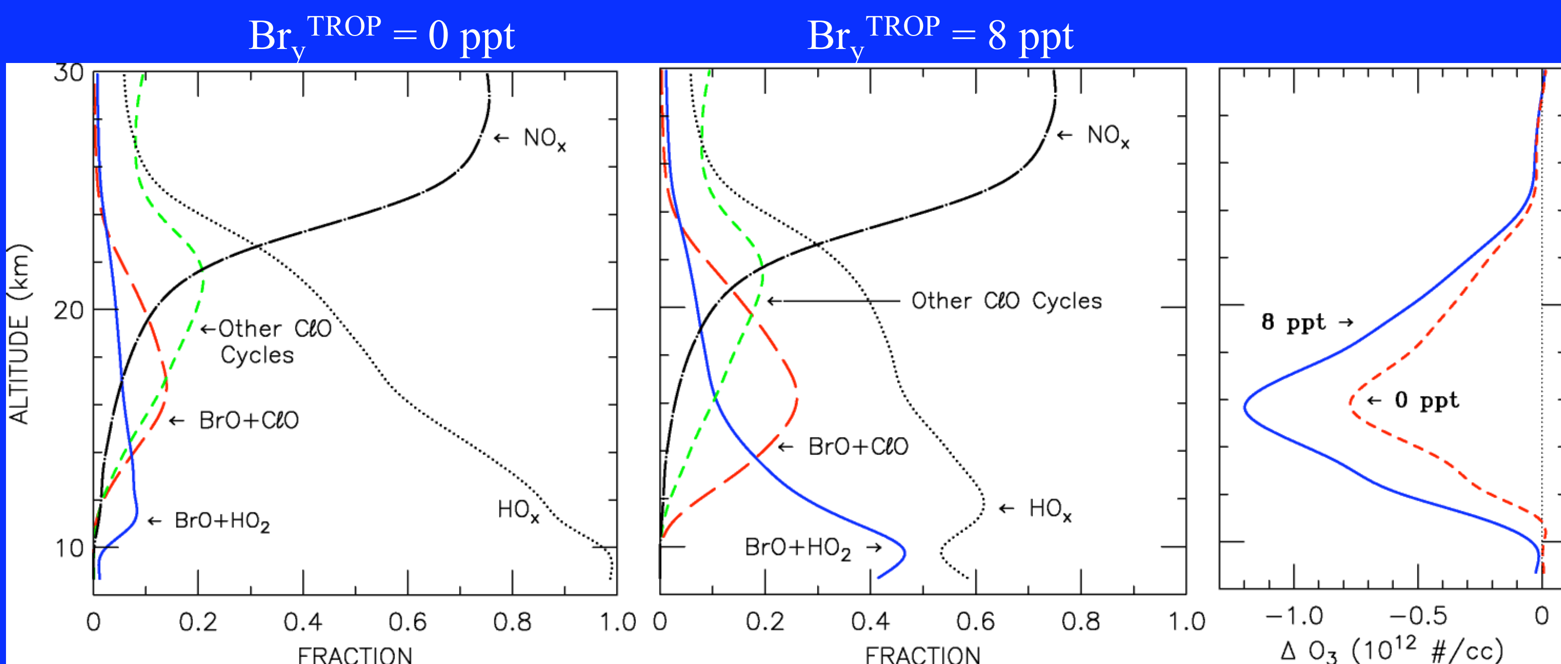




10
30
100
300
1000
Pressure (mb)
Subsidence
20km
16km
9km
Altitude
Large-scale ascent
400K
380K
350K
330K
300K
Pole
Latitude
Equator

Ozone Photochemistry

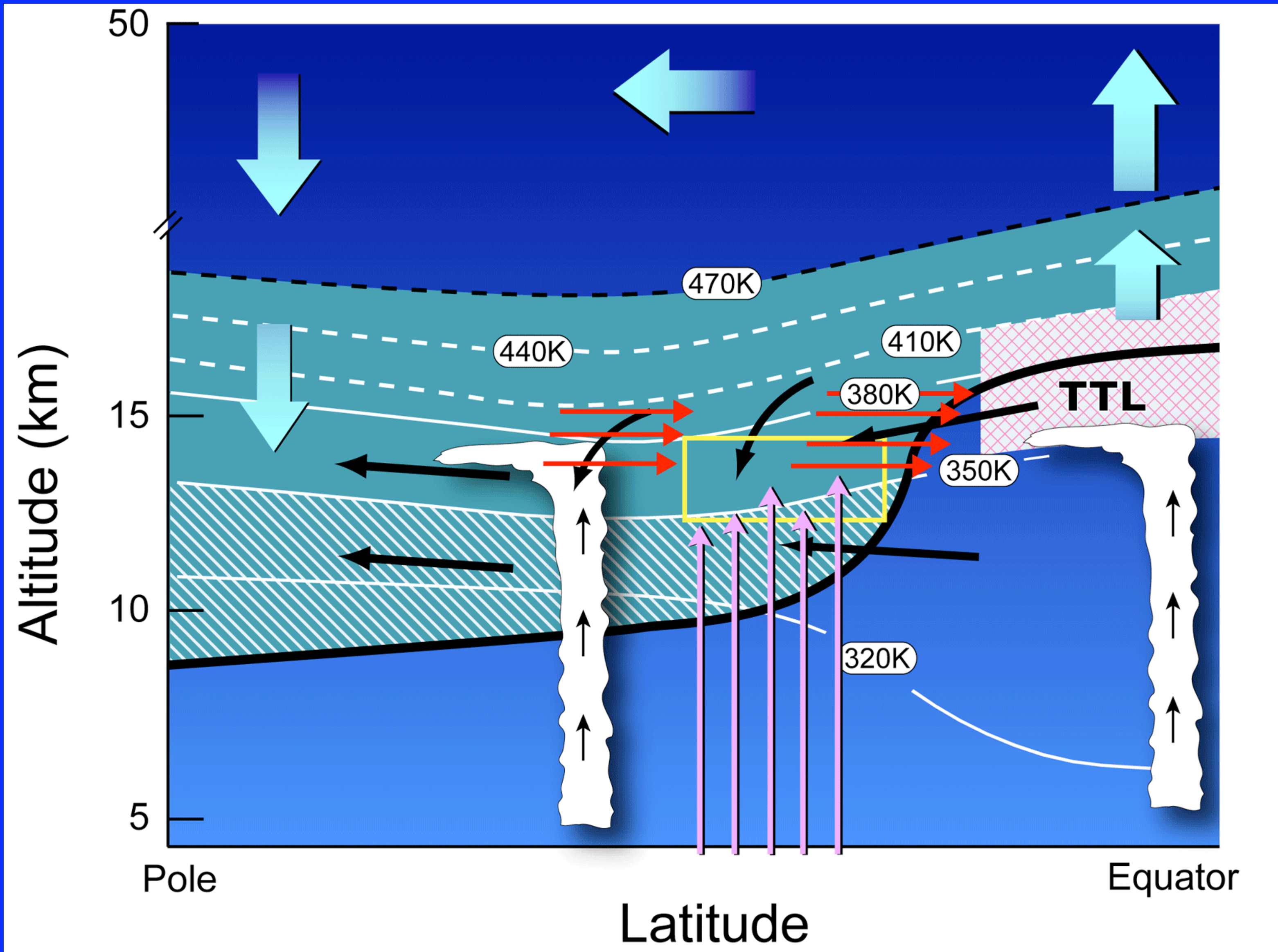
AER Model Time Slice: 47°N, March 1993

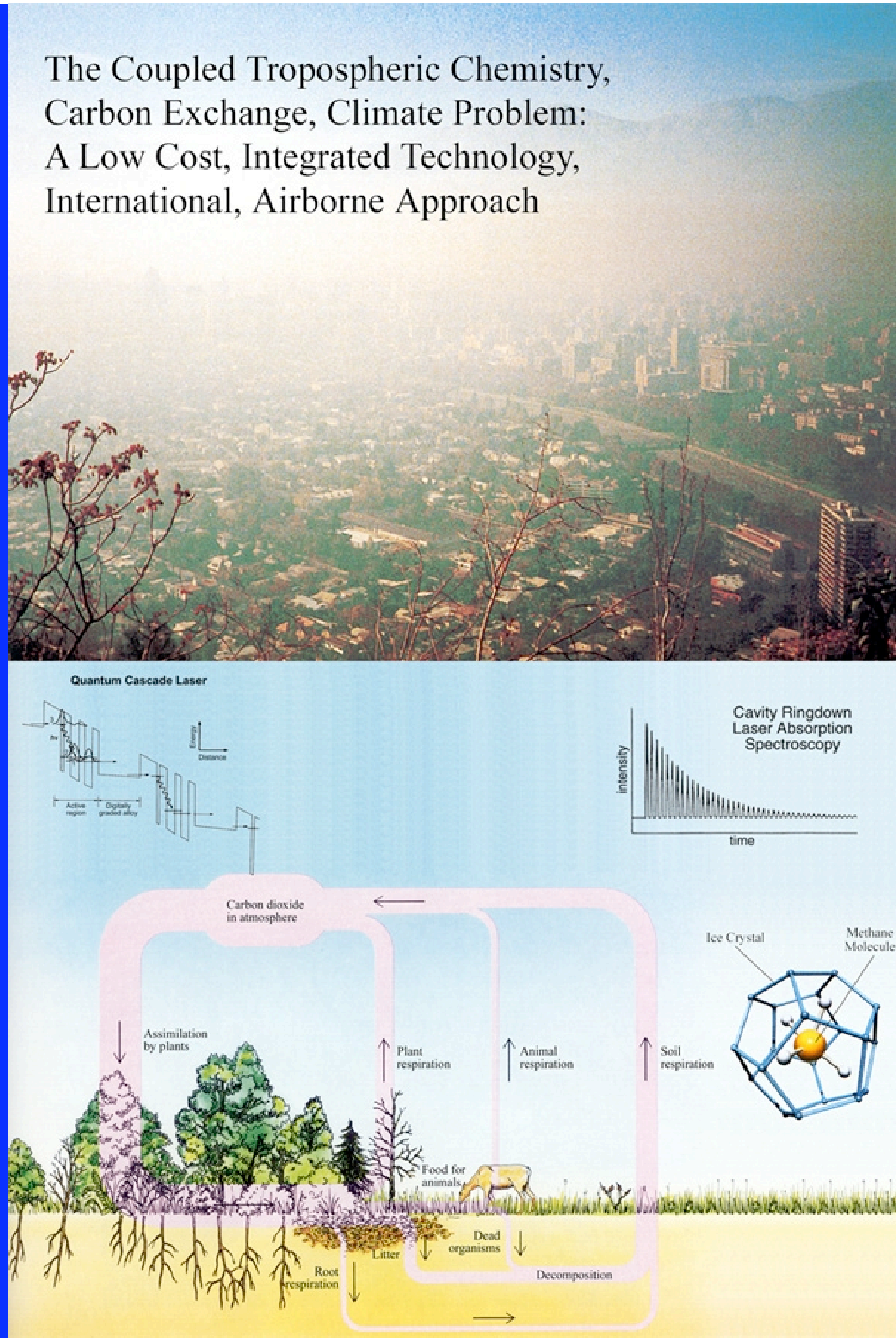


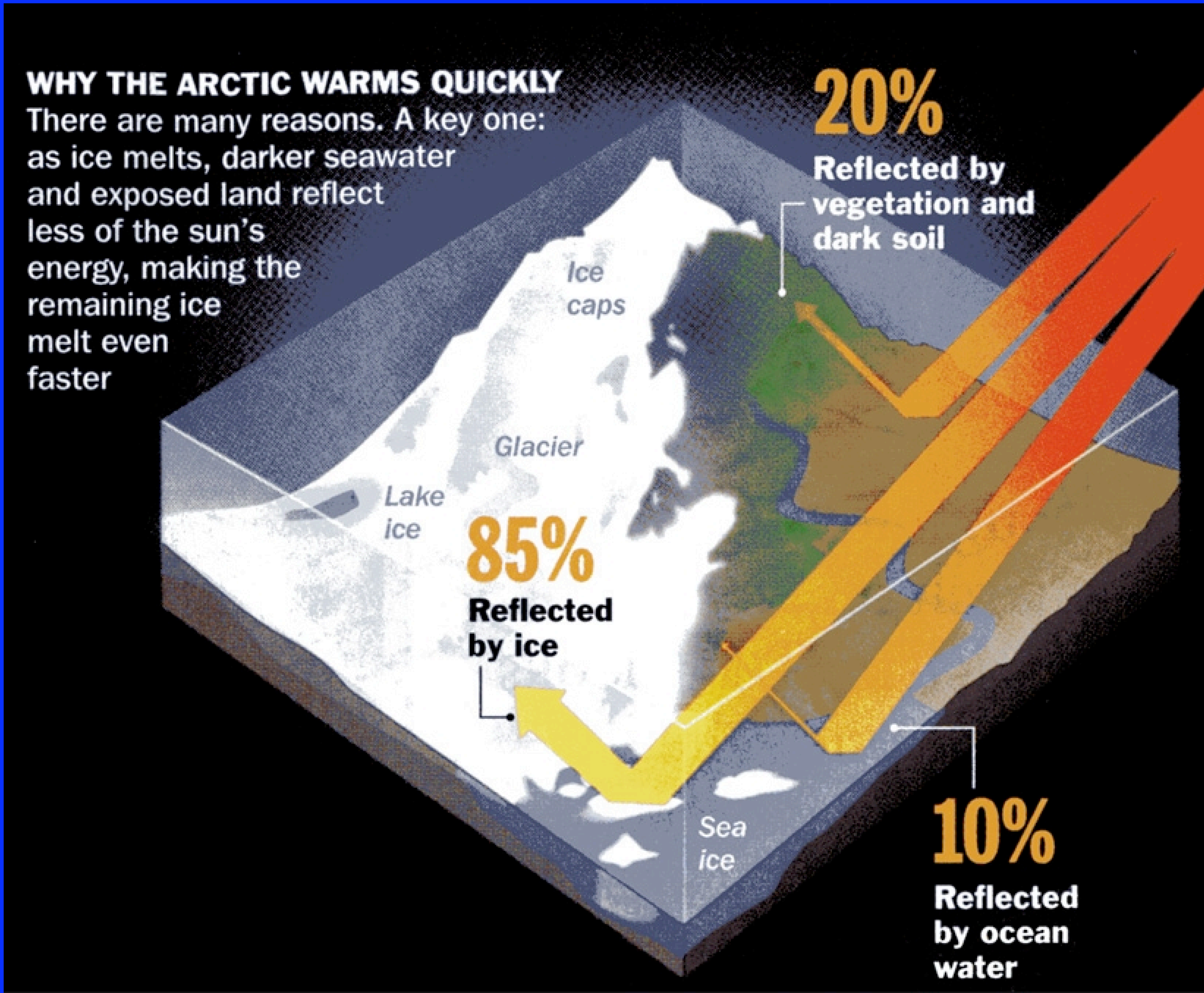
Enhanced Bromine:

- ↑ ozone depletion due mainly to BrO+ClO cycle
- $BrO+HO_2$ cycle becomes significant O_3 sink below 16 km

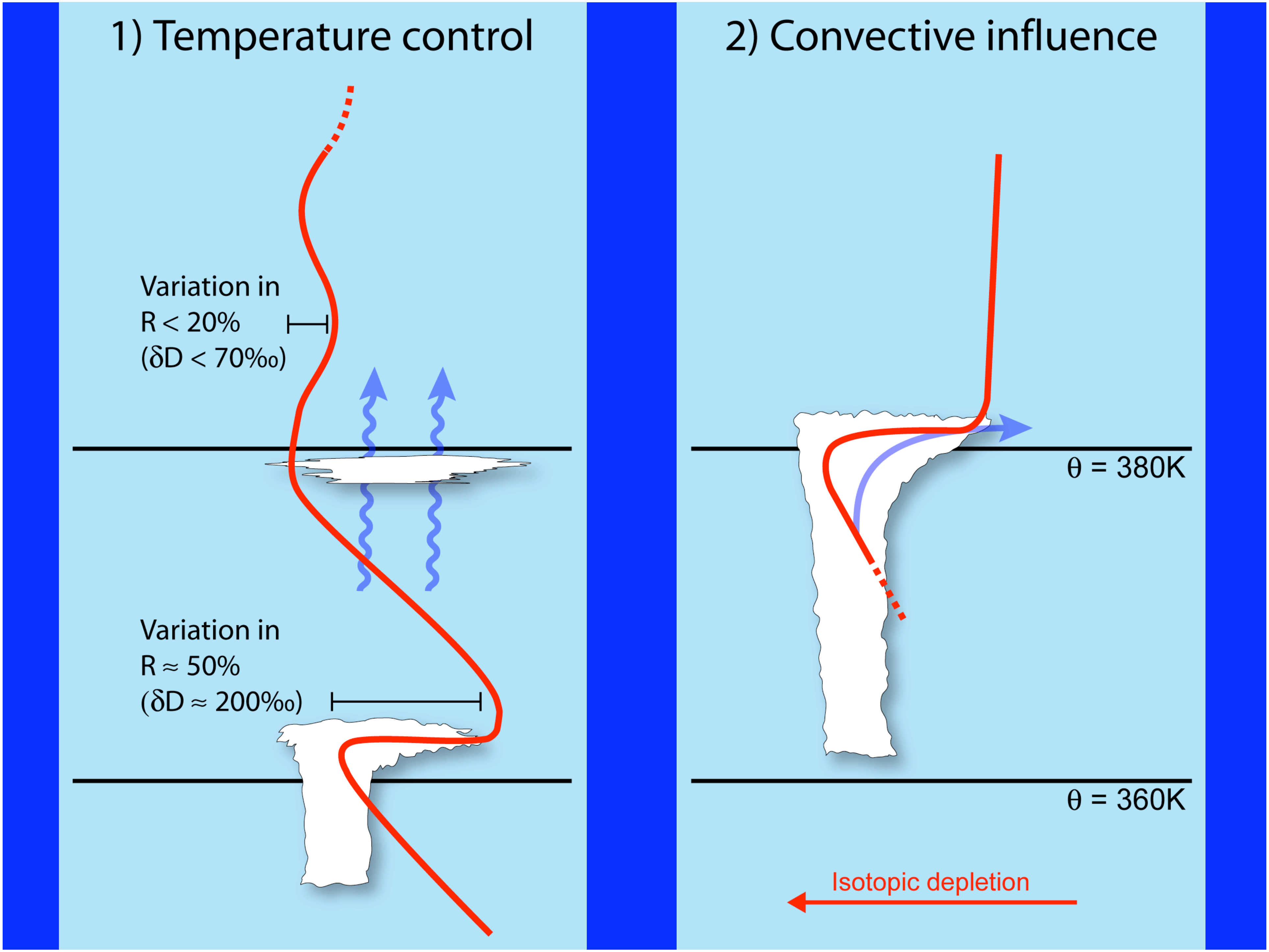
(BrO+HO_2 does not drive O_3 depletion if Br_y^{TROP} is constant over time)


50
15
10
5
Altitude (km)
470K
440K
410K
380K
350K
320K
TTL
Pole
Equator
Latitude


The Coupled Tropospheric Chemistry,
Carbon Exchange, Climate Problem:
A Low Cost, Integrated Technology,
International, Airborne Approach
Quantum Cascade Laser
Cavity Ringdown Laser Absorption Spectroscopy
intensity
time
Carbon dioxide in atmosphere
Ice Crystal
Methane Molecule
Assimilation by plants
Plant respiration
Animal respiration
Soil respiration
Food for animals
Dead organisms
Litter
Root respiration
Decomposition

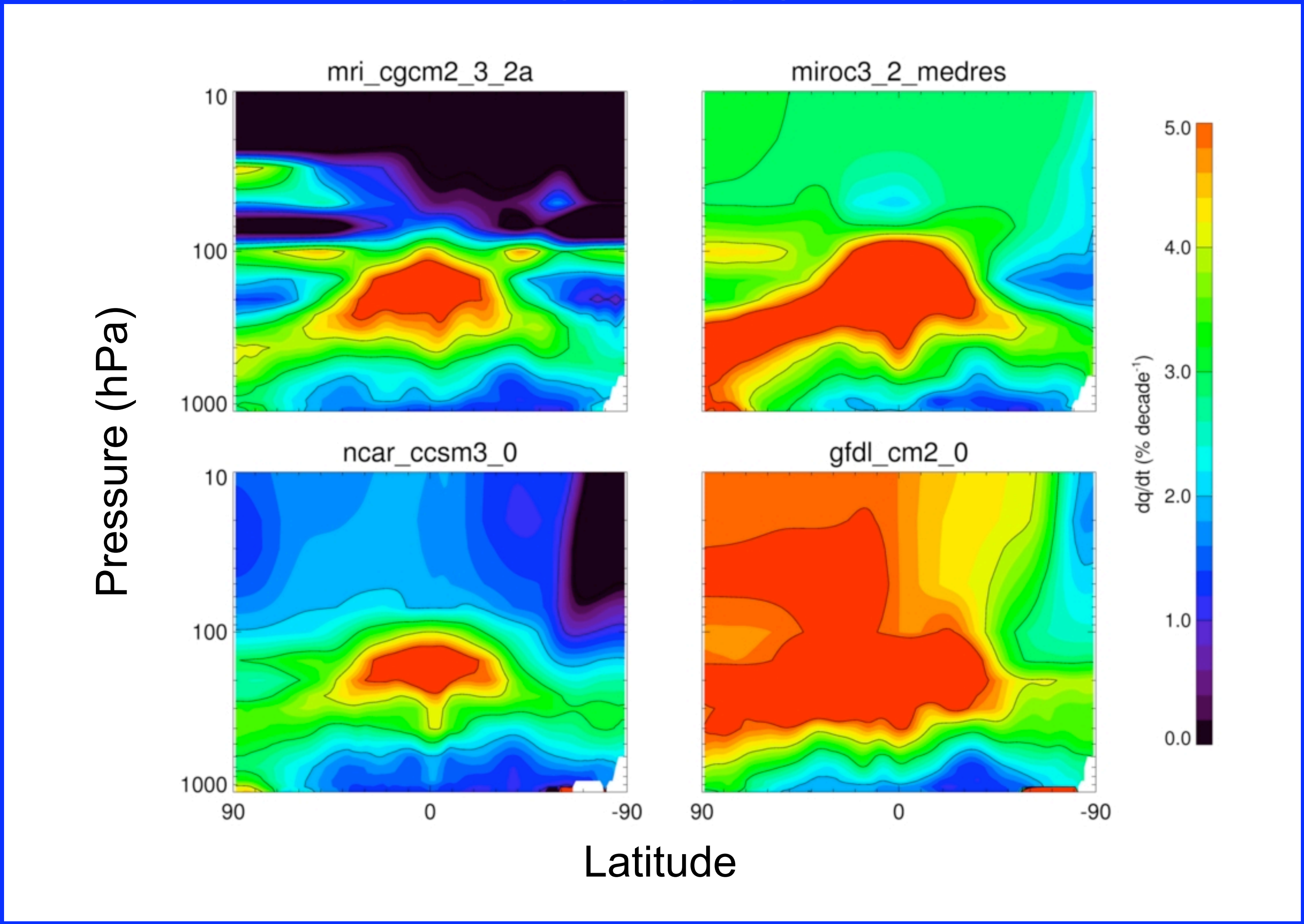

WHY THE ARCTIC WARMS QUICKLY
There are many reasons. A key one: as ice melts, darker seawater and exposed land reflect less of the sun's energy, making the remaining ice melt even faster
20%
Reflected by vegetation and dark soil
Ice caps
Glacier
Lake ice
85%
Reflected by ice
Sea ice
10%
Reflected by ocean water


Proposed Altair Payload
Pressure
Temperature
Telemetry/GPS
Cloud/Particle
LIDAR
ALTAIR
Tracer Measurements
Methane (DFG/Herriott)
N_2O (QC/Herriott)
Carbon Dioxide (DFG/Herriott)
Carbon Monoxide (QC/Herriott)
Formaldehyde (Fiber/CRDS)
Water (Lyman Alpha)
Total Water (Lyman Alpha)
Water (DFB/Herriott)
Ozone (UV Absorption)
H_2O/HDO (ICOS or Fragmentation LIF)
Radical Measurements
OH (Ti:Saph/LIF)
HO_2 (Ti:Saph/LIF)
NO_2 (Ti:Saph/LIF)
ClO/ClOOCl/ClONO2 (RF)
BrO/BrONO2 (RF)
IO (Ti:Saph/LIF)



1) Temperature control
Variation in
R < 20%
(δD < 70‰)
Variation in
R ≈ 50%
(δD ≈ 200‰)
2) Convective influence
θ = 380K
θ = 360K
Isotopic depletion

IPCC 4AR dq/dt: Difference Between Model Forecasts



Water Isotopologues: Motivation

- Study of dehydration mechanisms (response to forcing)
- Priority 1 measurement for upcoming science missions
- Development need has been identified
  - Instrument for vapor phase is needed
  - Science requirements demand improved sensitivity
- Direct absorption:
  - simultaneous measurement of H_2O, HDO, $H_2{}^{18}O$
- **Substantial pathlength enhancement:**
  - **Integrated Cavity Output Spectroscopy (ICOS): > 4km pathlength**

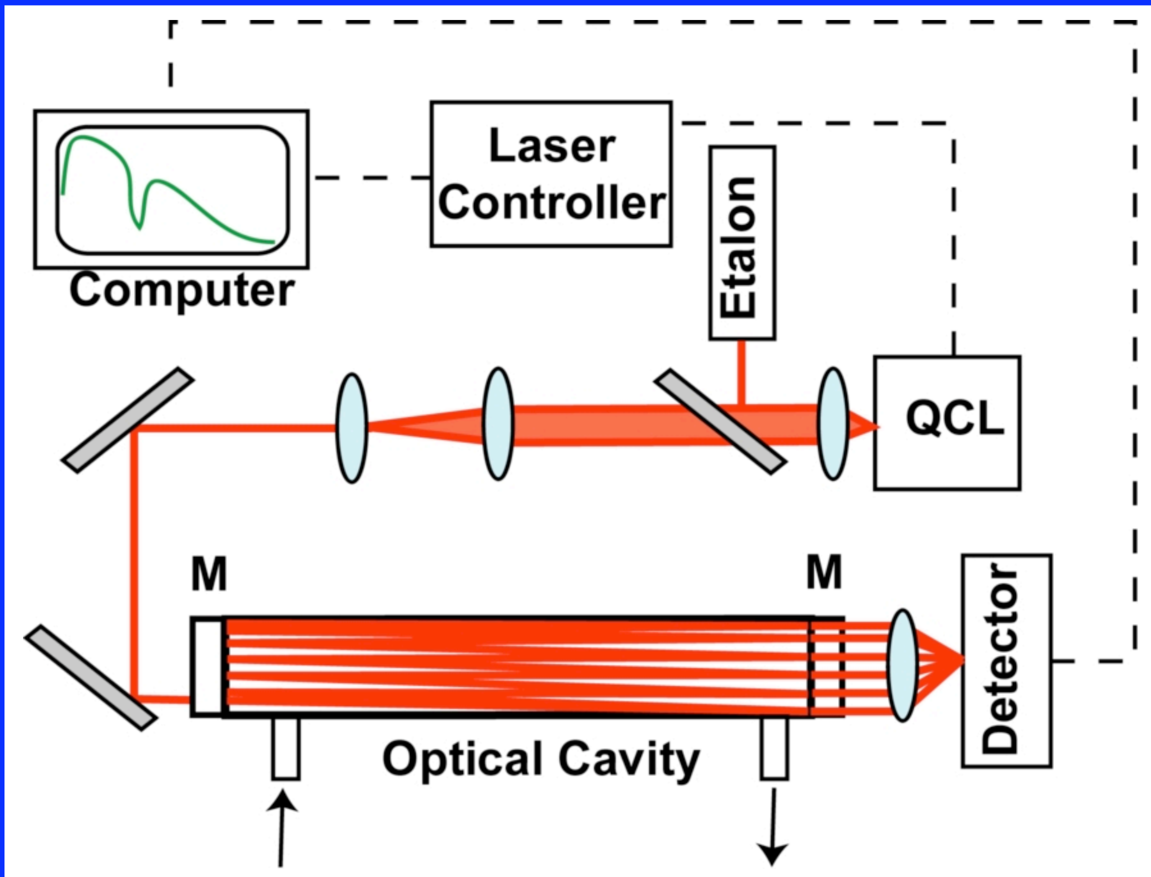
HDO measurement requirements

	Science needs
Sensitivity *in: Integration time* *or: Spatial scale*	~ 50 ppt 3 s 600 m
Precision	3 % per species (20-25 ‰ in δD)
Accuracy	3 % per species
Hysteresis time	< 3 s

Design of the mid-IR ICOS Flight Instrument for Measurement of HDO, $H_2^{18}O$, and H_2O

- **Optical System:**
  - **Maintain sensitivity in transfer to robust and compact flight design**
- **Gas Sampling System:**
  - **Particle free sampling, minimization of wall effects and trapped volumes, constant P in ICOS cell**
- **Thermal Management:**
  - **Constant T of optical system and of gas volume in cell**
- **Electronics:**
  - **Compact design for a low pressure environment**
- **Software:**
  - **Algorithms for robotic control of flight instrument, data acquisition and post-flight data reduction**

Integrated Cavity Output Spectroscopy (ICOS)



$$\frac{dI}{dt} = T \times P - I\frac{c(1\text{-}R + \acute{a} \times L)}{L}$$

$$I_{SS} = \frac{PTL}{c(1 - R + \acute{a}?L)}$$

$$\tau = \frac{L}{c(1\text{-}R+\acute{a}?L)}$$

$$L_{eff} = \frac{L}{1 - R}$$

$$L_{eff} = \frac{L}{1\text{-}0.9998} = 5000L$$

- Steady State cw transmission monitored
- Ideal for measuring multiple species
- **Substantial pathlength enhancement:** **4200 m**

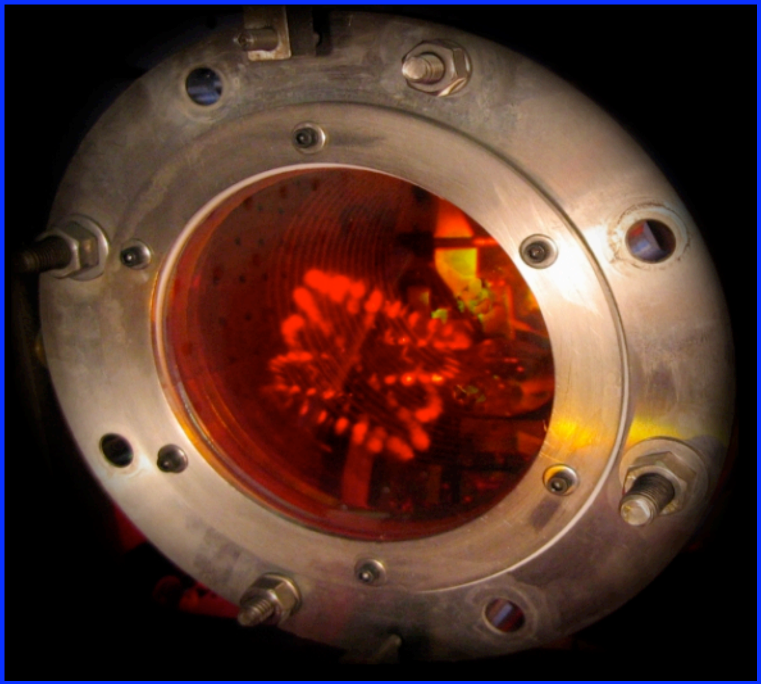
[1]Paul *et al.* Appl. Opt. **40**, 4904 (2001); Baer *et al.* Appl. Phys. B **75**, 261 (2002) .

Off-axis ICOS[1]

- On-axis alignment gives high “noise” from cavity resonances
- Off-axis alignment reduces cavity resonances
- Passive cw technique with unsurpassed sensitivity (30 km pathlength)

[1]Engel, Keutsch *et al*. in preparation (2005).

Off-axis ICOS



- On-axis alignment gives high “noise” from cavity resonances
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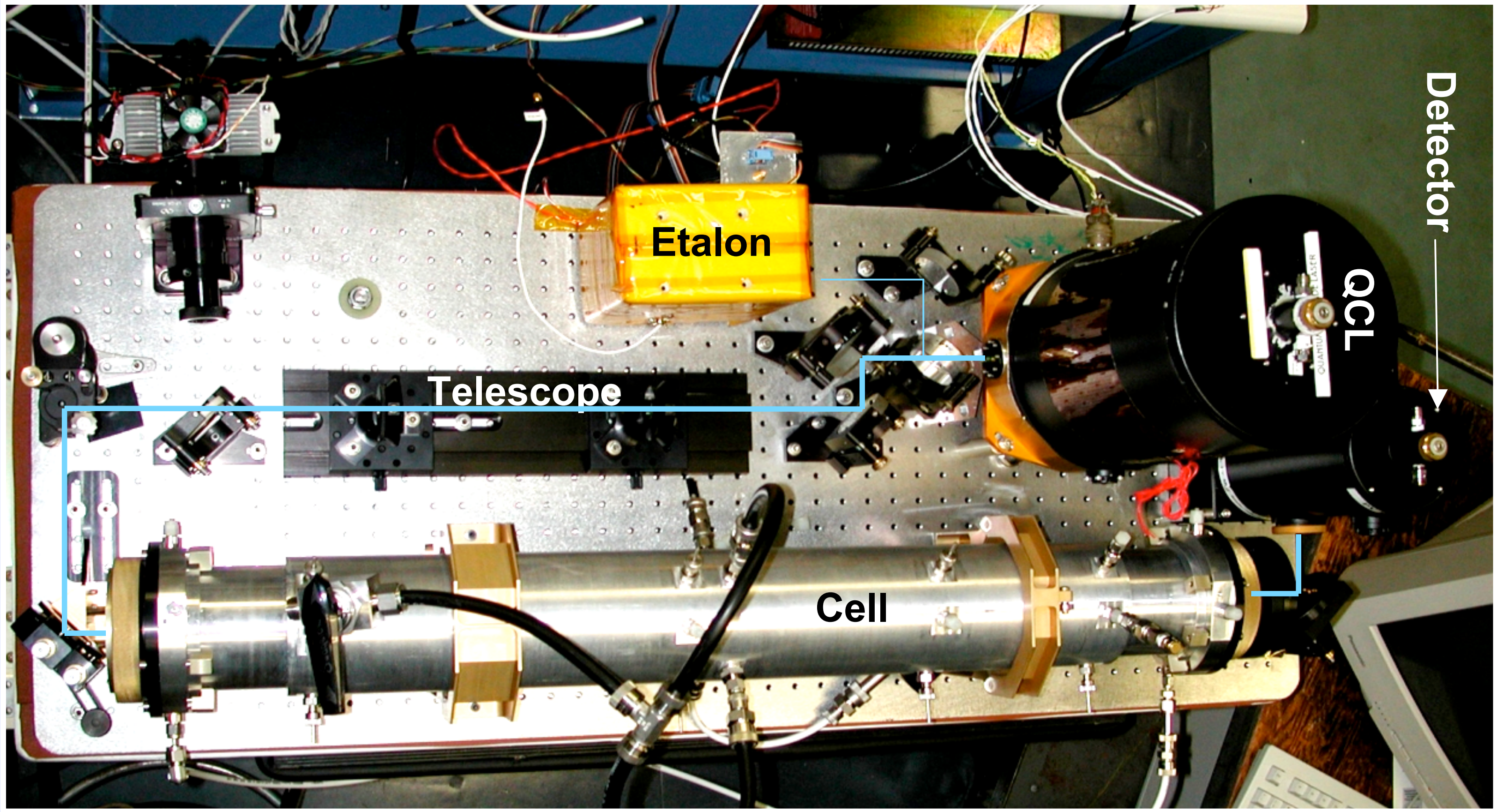
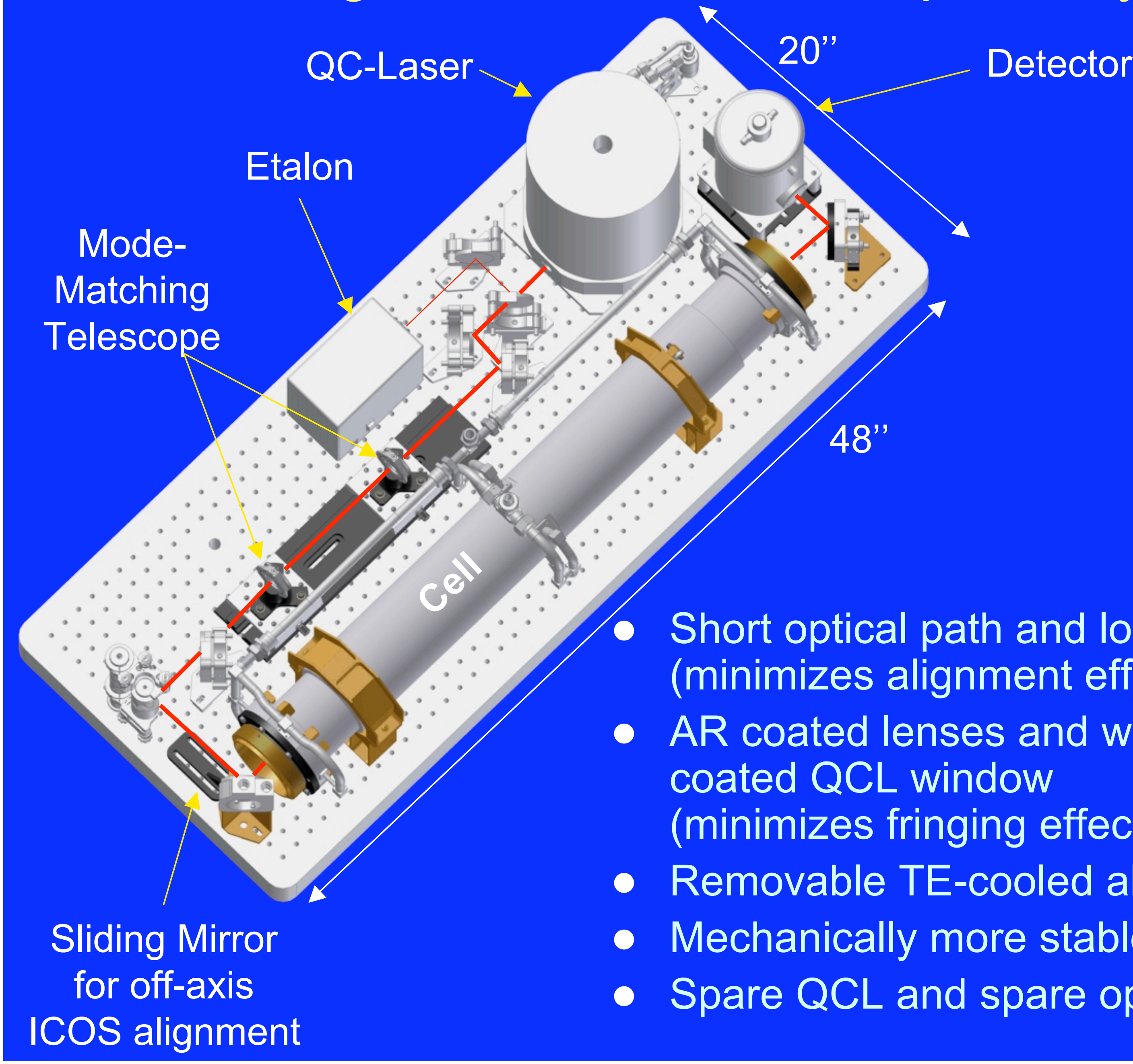
- Passive cw technique with unsurpassed sensitivity (30 km pathlength)

Harvard ICOS instrument



[1]Moyer, E.J., Sayres, D.S., Keutsch F.N. *et al.* in preparation (2005).

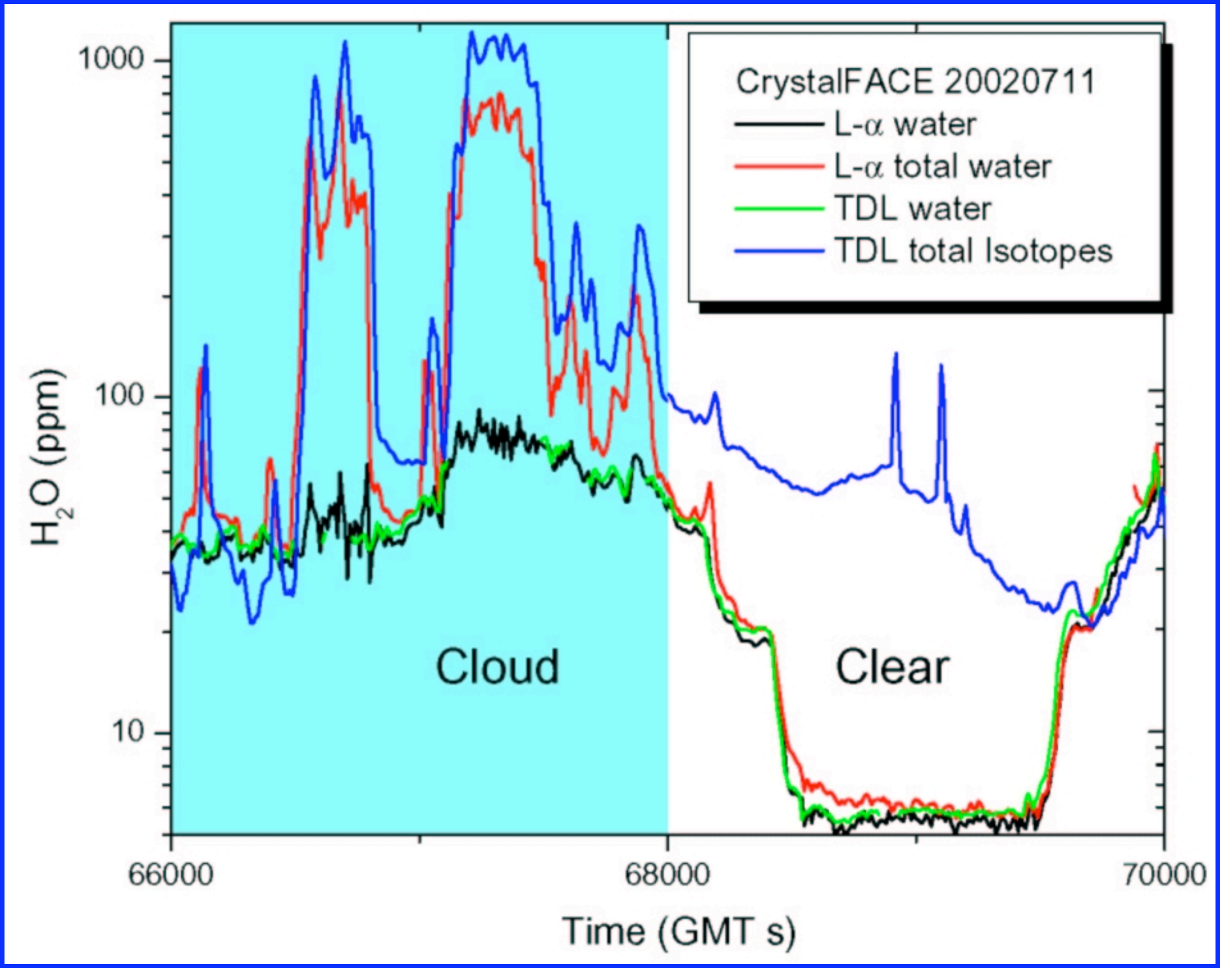
Flight Modifications of Optical System

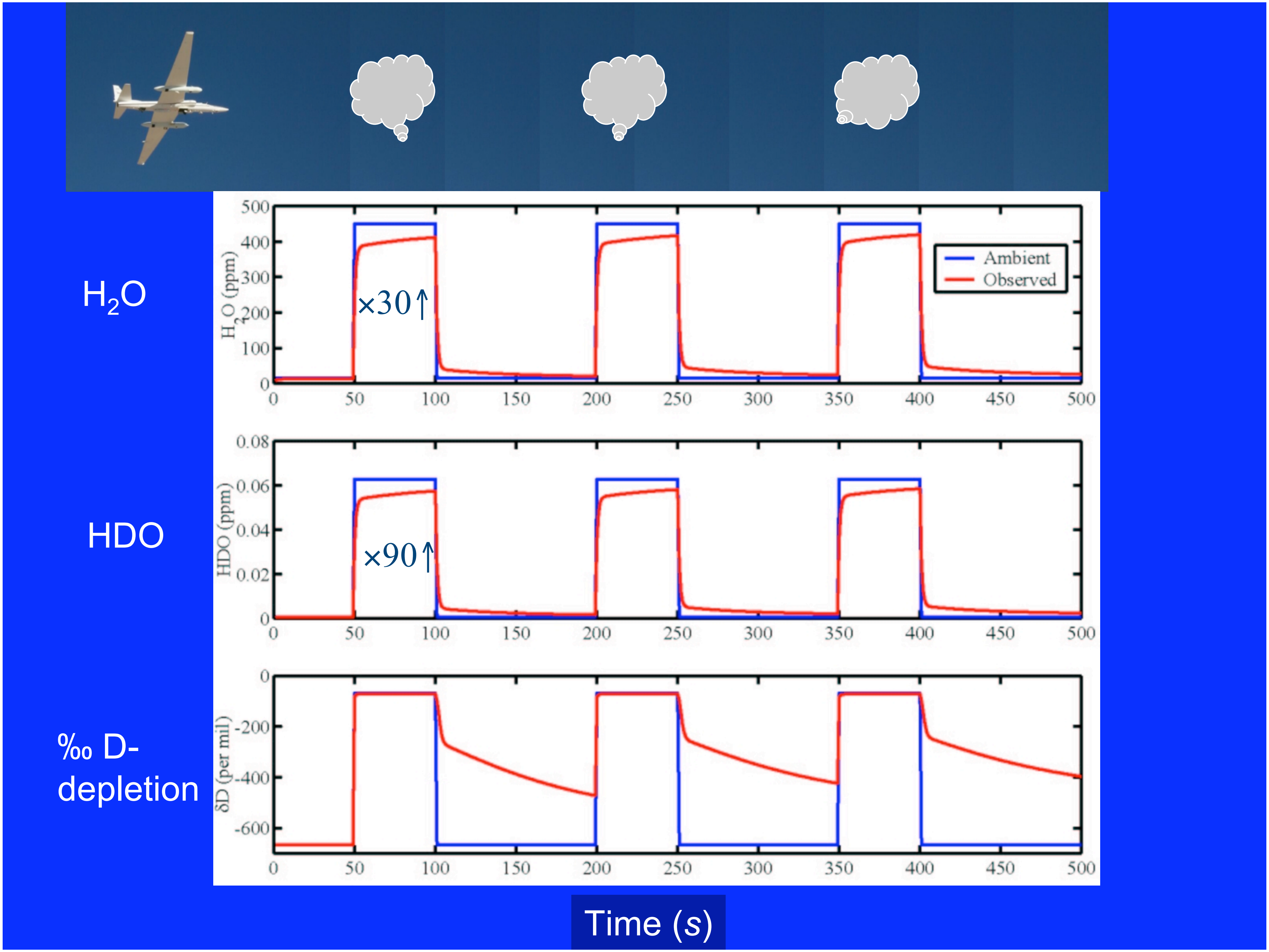


- Short optical path and locking optical mounts (minimizes alignment effects of vibrations)
- AR coated lenses and wedged and AR coated QCL window (minimizes fringing effects)
- Removable TE-cooled alignment laser
- Mechanically more stable optical cell
- Spare QCL and spare optics

Motivation: In situ water isotope instruments require validation

- We expect instrument artifacts to contaminate water measurements.
  - Sampling
  - Optical
  - Software analysis
- Independent measurements can help identify artifacts.



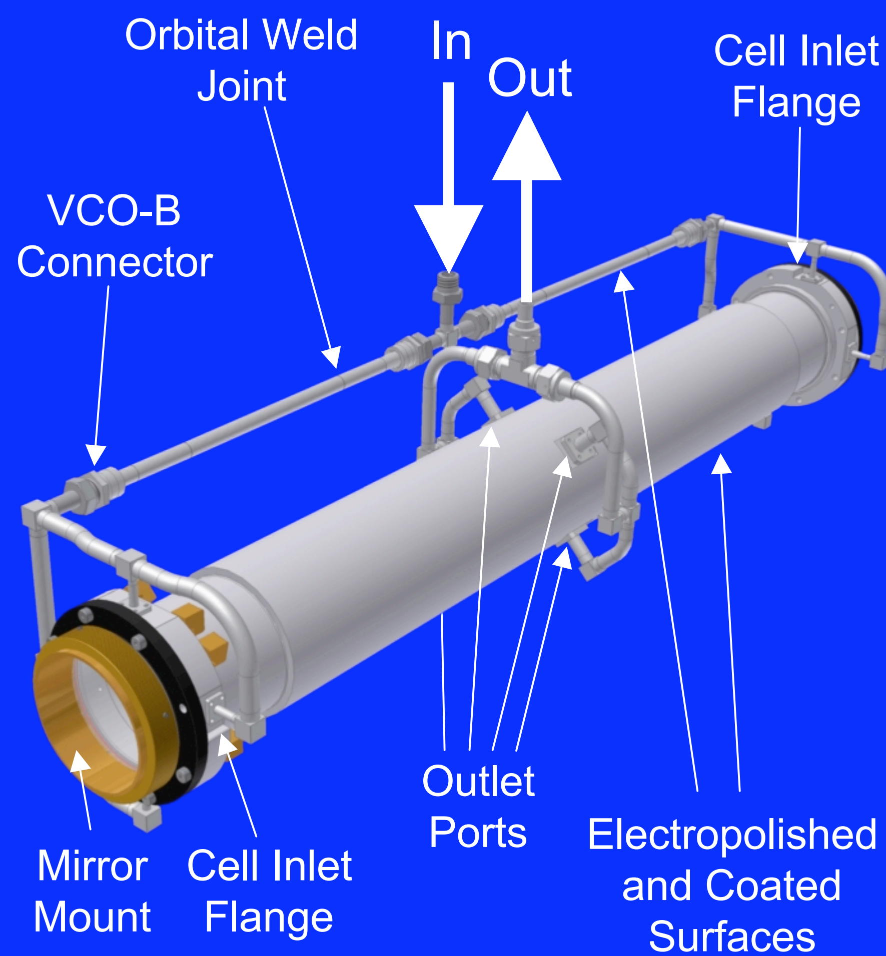


H_2O
HDO
‰ D-depletion
H_2O (ppm)
HDO (ppm)
δD (per mil)
×30↑
×90↑
Ambient
Observed
0
50
100
150
200
250
300
350
400
450
500
0.08
0.06
0.04
0.02
-200
-400
-600
Time (s)

Design of ICOS Flight Cell

Flight Modifications: Accommodating Optical and Sampling Considerations

- Novel design of cavity with parallel mirrors and **NO** adjustable or moveable parts (vibration insensitive)
- Thermistors with high impedance and fast time response
- Electropolished and coated surfaces to minimize of wall effects
- Pharmaceutical grade connectors and valves, orbital weld joints, P-port placement and cell inlets/outlets designed to eliminate trapped volumes



Inlet Side:

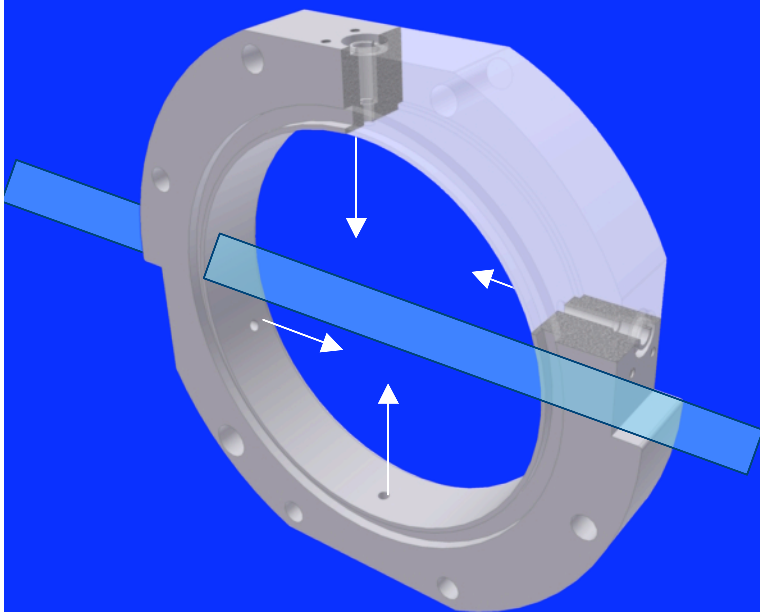
- Rear facing inlet for particle exclusion
- Heaters for gas, feedback to T_{gas} in cell

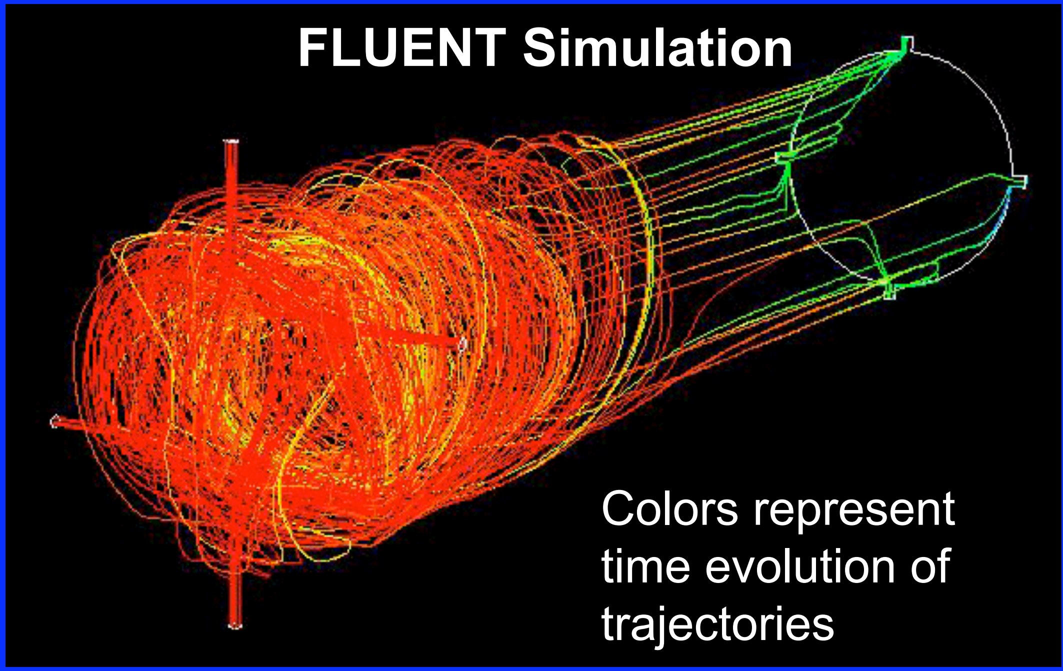
Outlet Side:

- Large diameter tubing, high throughput
- Scroll Pump: oil-free to protects mirrors flush time of ca. 3s

ICOS Cell Gas Inlet Design

Inlet ports are located asymmetrically



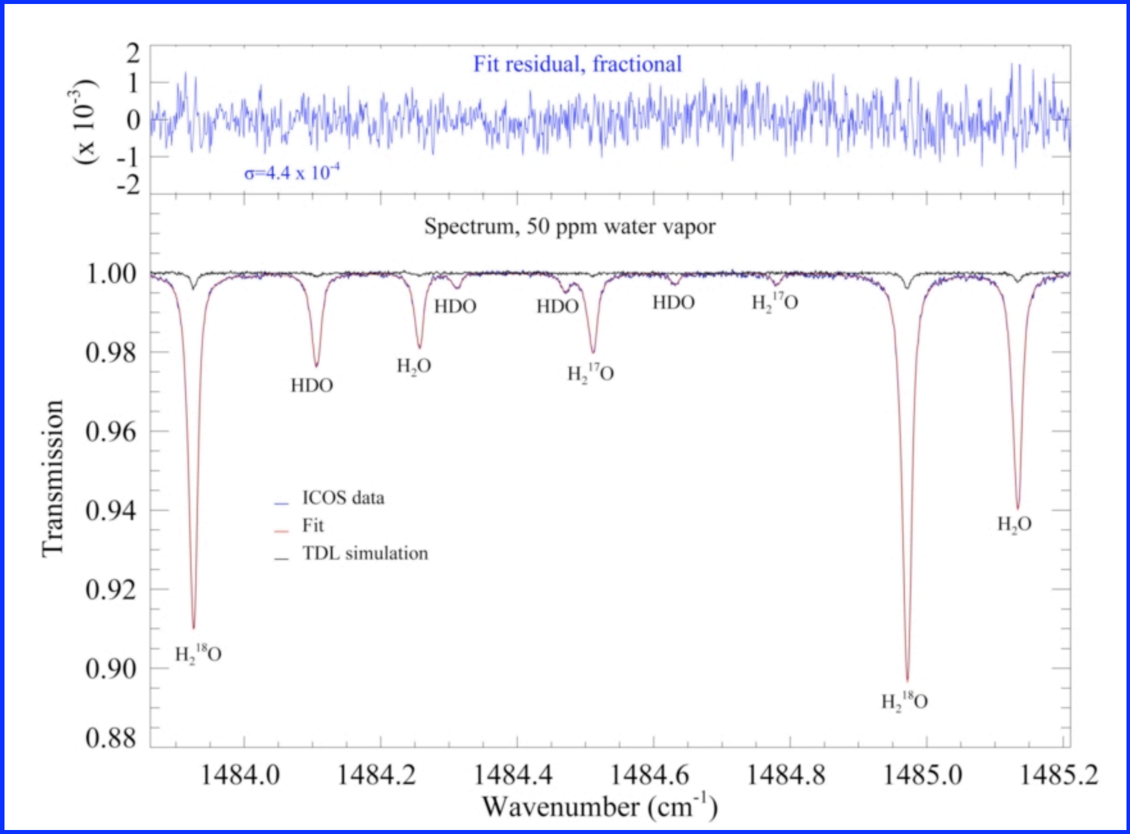


Flight Modifications

- Inlet into gas cell results in swirling gas flow
- Pump ports are in center of cell
- Design excludes P gradients and stagnant region in front of mirrors

Fit algorithm yields measurement precision comparable to noise-equivalent absorption

- SNR on the spectrum is > 50, and both fit residual and derived mixing ratio yield similar values.
- Integration time here is ½ s, 6 x shorter than flight integration times. Projected flight SNR is > 130 in these conditions.
- Increased data acquisition rate and fit improvements should allow further increases in SNR by a factor of 5-10.
- Stratospheric SNRs are more than sufficient for relevant science issues.



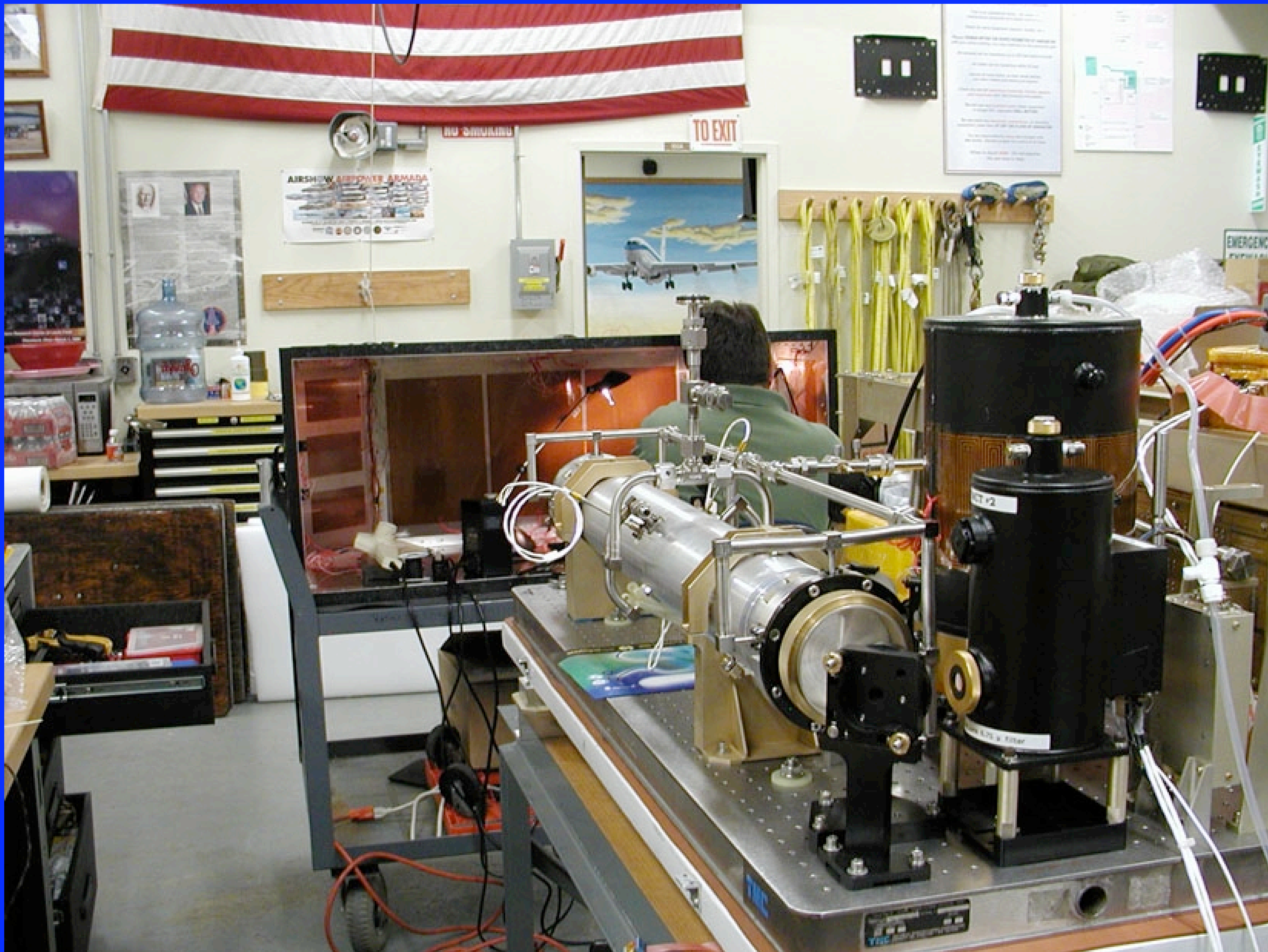
Synthetic spectrum in black represents the signal obtained by traditional tunable diode laser absorption spectrometers in the same conditions. The long ICOS optical pathlength produces deeper absorption lines.

Laboratory technique → flight instrument:

- Target molecule: HDO (and H_2O, $H_2^{18}O$)
- Platform: NASA's WB57-F high-altitude aircraft
- Test flights: November 2004
- Validation strategy: comparison with simultaneous observations of HDO and H_2O by 3 other independent instruments

HDO chosen because of:

- High scientific importance (priority 1 for Aura science missions)
- No adequate existing technology for stratospheric measurements
- ICOS can meet science needs

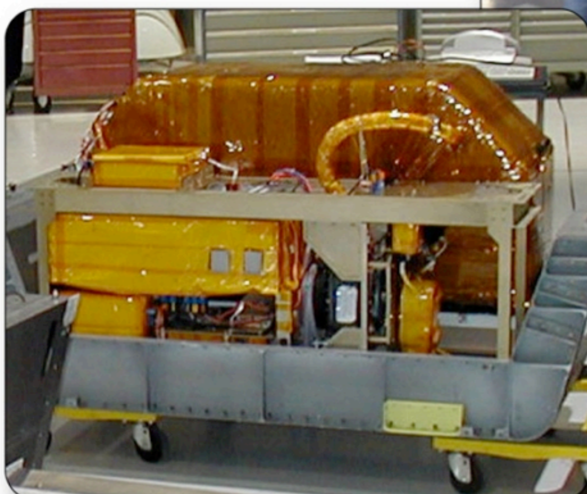

TO EXIT
EMERGENCY

Ly-α Water Vapor

H_2O

HOxotope

H_2O, HDO



Total Payload

ICOS

H_2O, HDO, $H_2{}^{18}O$, CH_4

Ly-α Total Water

H_2O (vapor + condensate)


Test flight results

Debut flights for two new water isotope instruments

Independent techniques, complementary strengths

ICOS Isotope Instrument

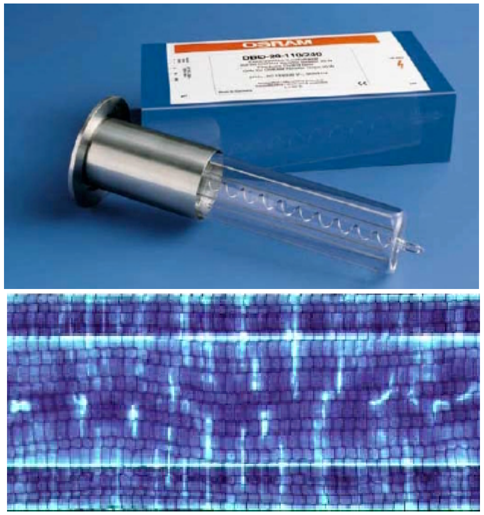
- Mid-IR absorption spectroscopy using new cavity-based technique
- *(Integrated cavity output spectroscopy)*
- Enhanced sensitivity (x 40) because of 4 km optical path
- Multiple species (H_2O, HDO, $H_2{}^{18}O$, $H_2{}^{17}O$, CH_4)

HOxotope Instrument

- Photofragment laser-induced fluorescence of OH and OD
- *(Heritage of Harvard HOx instrument)*
- Contamination-free sampling (HO_X radicals lost on wall contact)
- Improved sensitivity (x 2-10) over conventional techniques

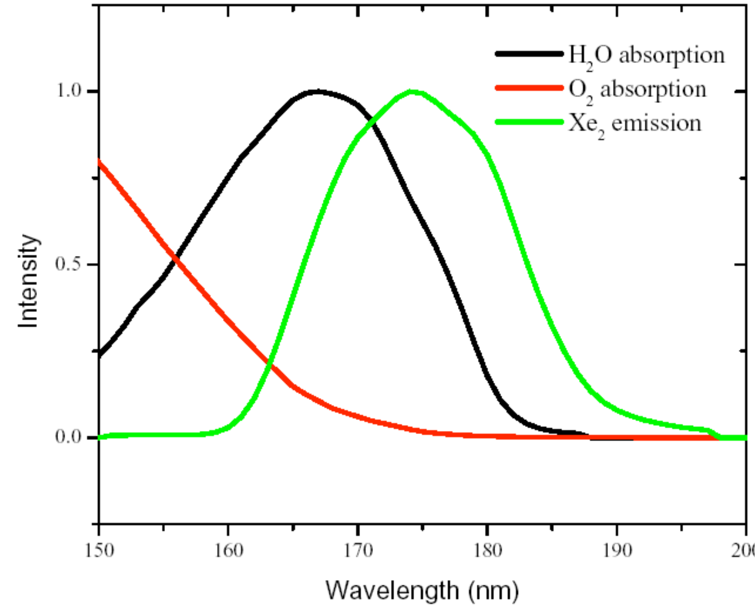
HOx isotopes:
Photolysis - Fluorescence detection of HDO/H_2O

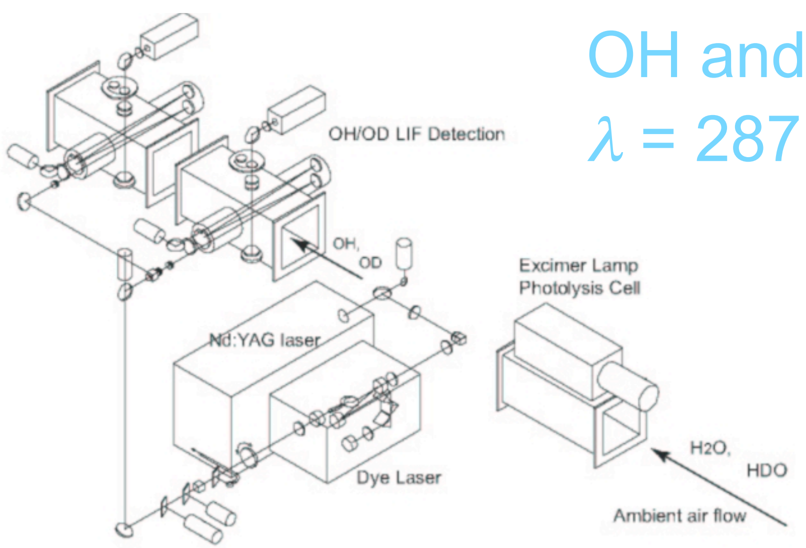
Excimer Lamp Photolysis



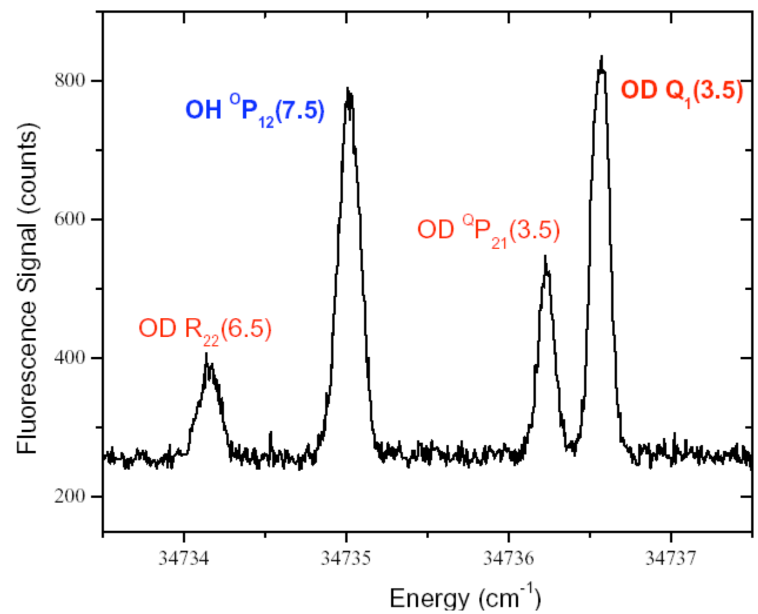
$H_2O + h\nu \rightarrow H + OH$
$HDO + h\nu \rightarrow H + OD$

$h\nu$ = 8W
λ = 172 nm



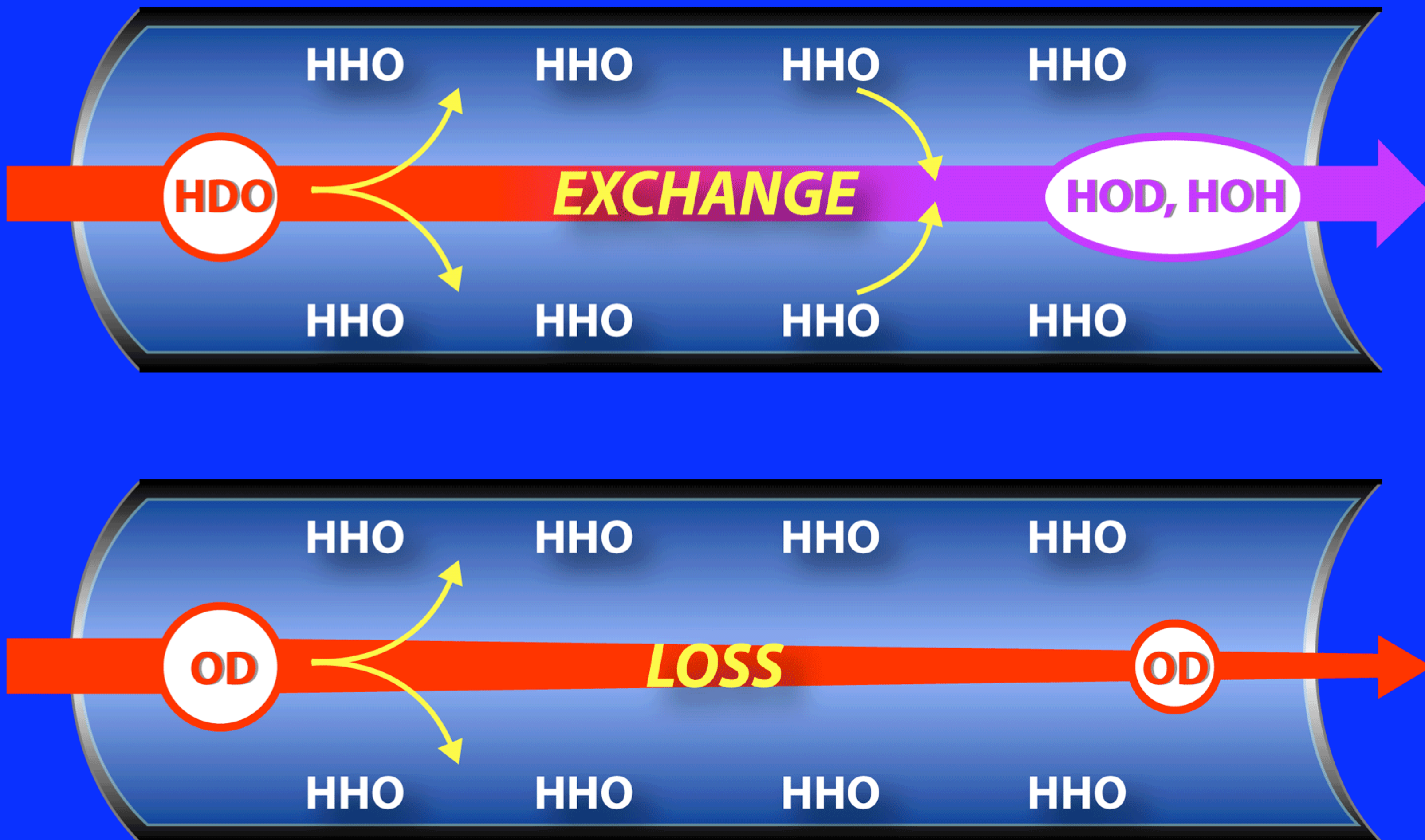


OH and OD LIF
λ = 287 nm

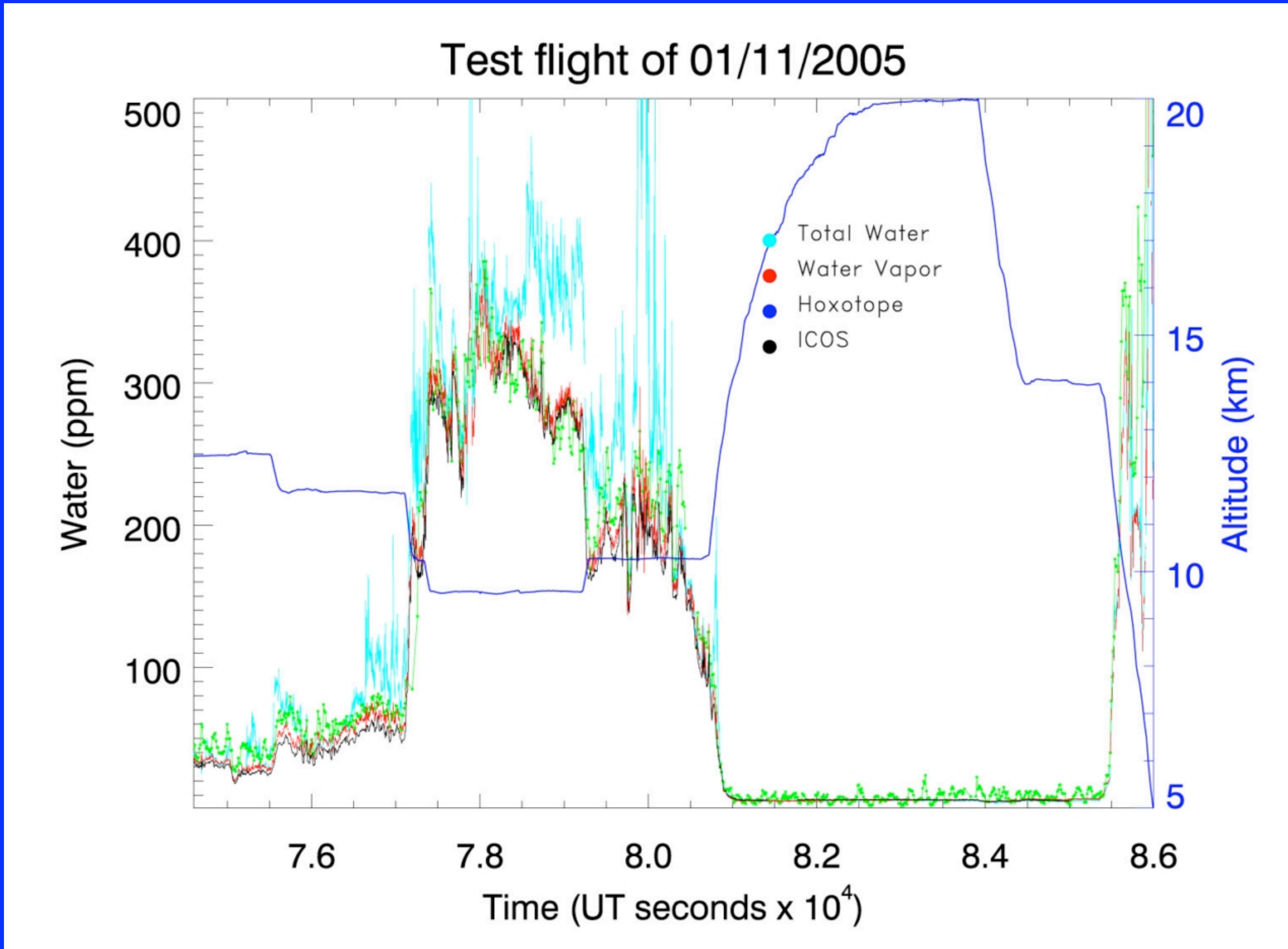


Radical vs. Molecular Sampling

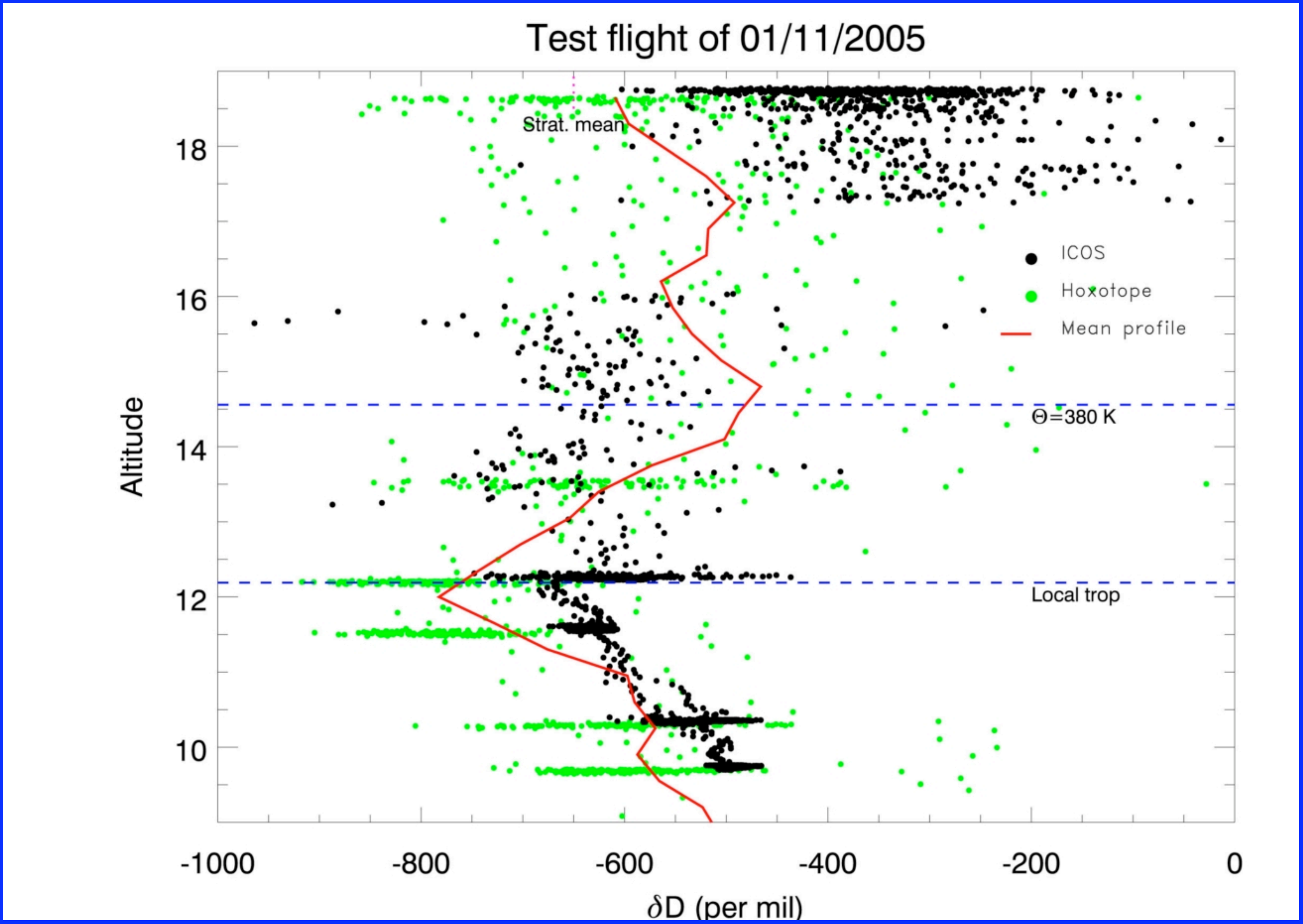
Molecular water exchanges with walls. OH and OD radicals are lost irreversibly



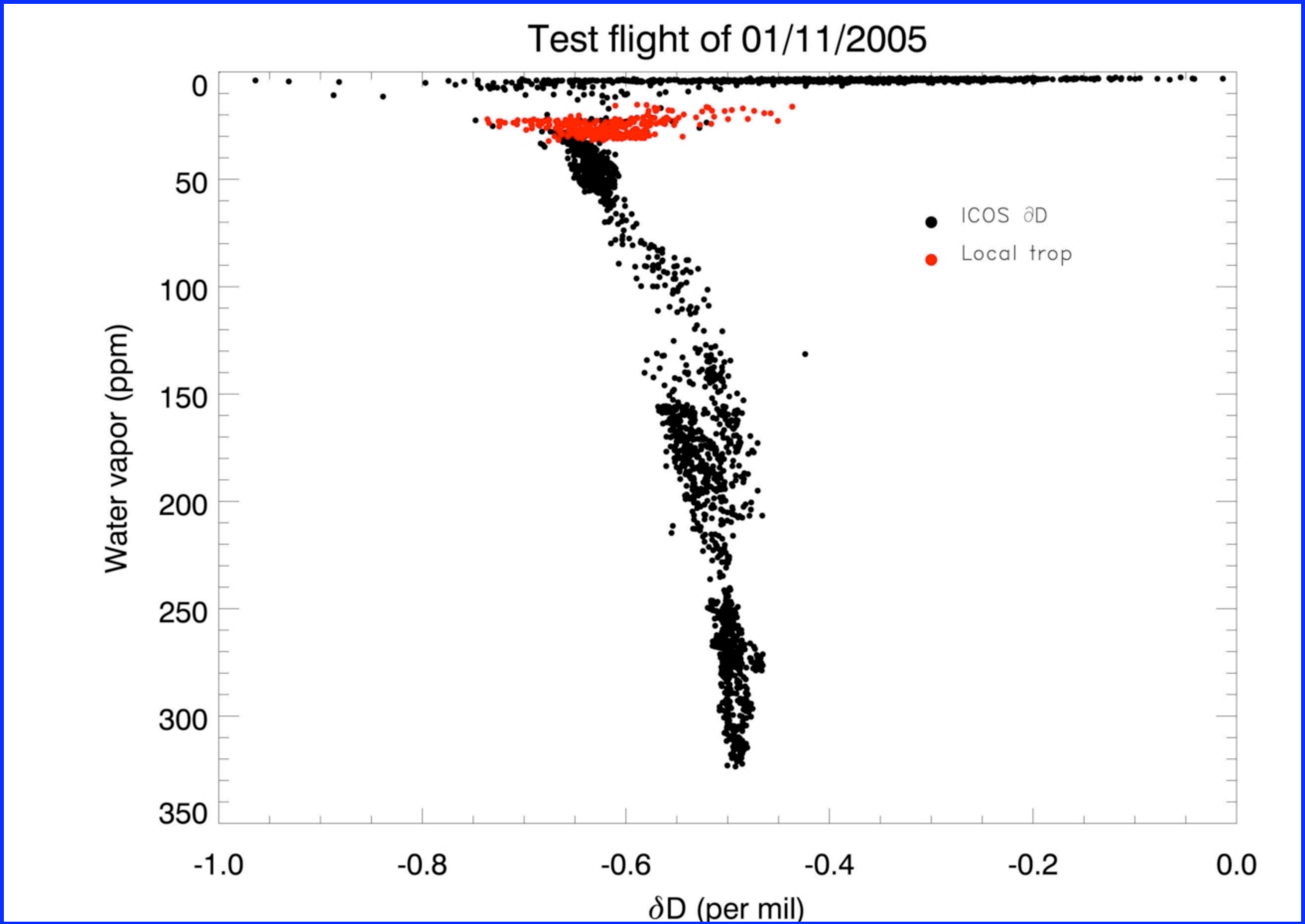
Consistency between all four instruments

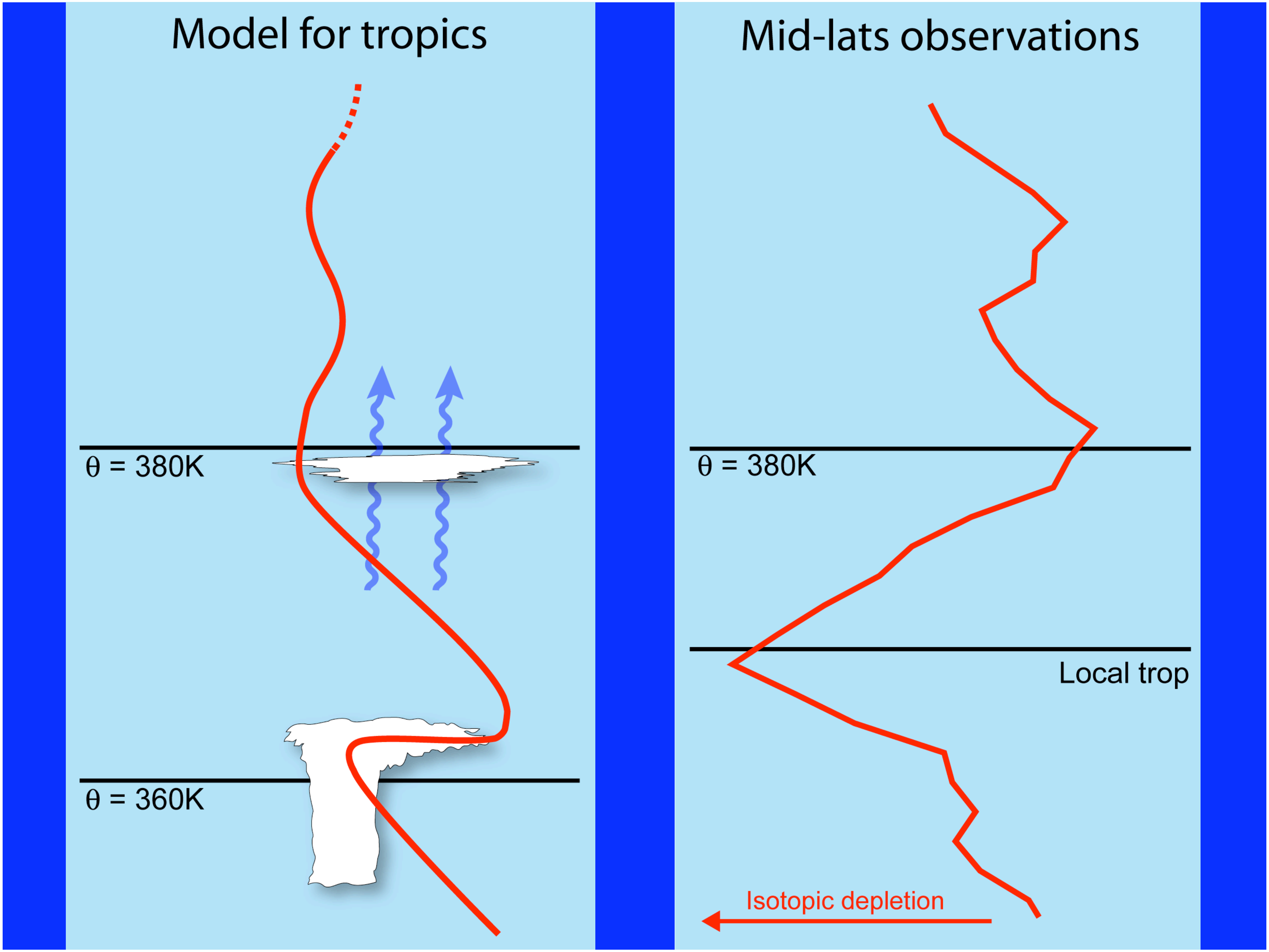


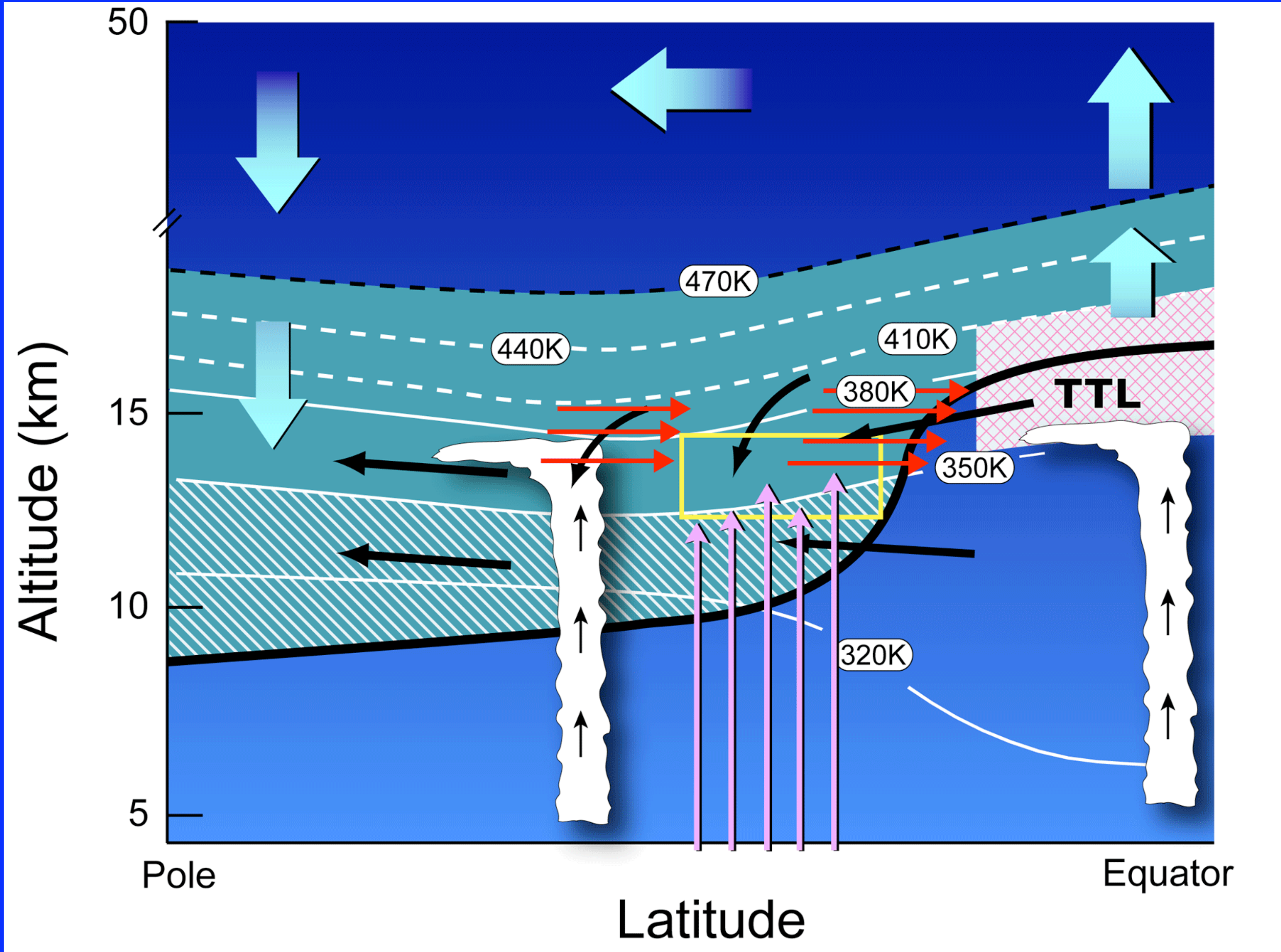
Vertical profiles are plausible



Tropospheric variation is not noise




Model for tropics
θ = 380K
θ = 360K
Mid-lats observations
θ = 380K
Local trop
Isotopic depletion



50
15
10
5
Altitude (km)
470K
440K
410K
380K
350K
320K
TTL
Pole
Equator
Latitude

HDO in-flight measurement capability

	Science needs	ICOS	HOxotope
Sensitivity *in: Integration time* *or: Spatial scale*	~50 ppt 3 s. 600 m	60 ppt 3 s. 600 m	250 ppt 10 s. 2 km
Precision	3 % (20-25 ‰)	3 %	---
Accuracy	3 %	---	---
Hysteresis time	< 3 s.	< 3 s. for cirrus	negligible

Conclusions: ICOS

- Most sensitive airborne mid-IR spectrometer
- Intercomparison with other instruments:
  - Fast time response
  - No evaporation of condensed phase
- Upgrades in progress:
  - Sealed cell
  - Pressure regulation system
- Water isotopologue (gas + condensed phase) measurements allow study of, e.g.:
  - Dehydration, transport, cloud microphysics and response to forcing
- Harvard ICOS instrument ready and available for Aura validation missions

Summary: HOxOTOPE

- Flight data high points:
  - Hoxotope worked as well in flight as in the lab
  - Fast time constant in H_2O and HDO sampling
  - Absence of unexplained artifacts
  - Good relative accuracy
  - Reasonable signal to noise (HDO ± 250 pptv/4s)
- Post flight schedule:
  - Calibration: 5% (50 per mil)
  - Sensitivity: factor of 5 for moderate effort
  - Investigate total water sampling mode

Development of Miniaturized Intra-Cavity DFG, and Pulsed Fiber-Optic Laser Systems